

REMARKS

These remarks are in response to the Final Office Action mailed January 12, 2011. The independent claims have been amended. Support can be found at page 25-26. No new matter is believed to have been introduced. The distances recited in the claims were previously search in the two prior responses and therefore do not introduce matter requiring any further search. The claims are supported by the specification and claims as previously examined.

Applicants respectfully thank Examiner Soderquist for the courteous interviews conducted with Applicants' representative, Joseph R. Baker, Jr., on October 21, 2011 and January 26, 2012. During the interview the Examiner indicated that evidence of the conductivity of polyaniline relative to phthalocyanine would assist in demonstrating the unexpected properties of the invention. More particularly, one of skill in the art would not expect a change in conductivity of a polyaniline by addition of other conductors due to polyaniline's inherently high conductivity. In contrast, phthalocyanine has a conductivity orders of magnitude lower than polyaniline. Accordingly, the Examiner indicated that such evidence would be persuasive in demonstrating that one of skill in the art would not combine the particular materials (e.g., conductive organic polymers such as polyaniline with other conductors).

Applicants provide excerpts from "Polymer Data Handbook," 1999, ed. James E. Mark, Oxford University Press (Exhibit A, attached hereto), which includes conductivity statistics for polyaniline (see, page 273) of 6.31-400 S/cm and 3×10^{-8} S/cm for phthalocyanine (see page 167)¹.

Additionally, Applicants and the Examiner discussed the distance of the 10-1000 angstroms recited in the independent claims and came to an agreement regarding the language.

¹ Note : Page 167 expresses the "electrical conductivity" as $\text{ohm}^{-1} \text{cm}^{-1}$, this is the inverse of the resistance which in fact is the same as S/cm.

I. REJECTION UNDER 35 U.S.C. §112, FIRST PARAGRAPH

Claims 98-110, 112-123 and 126-159 stand rejected under 35 U.S.C. §112, first paragraph as allegedly failing to comply with the written description requirement and lack of enablement. The claims allegedly contain subject matter which was not described in the specification in such a way as to enable one skilled in the art to which it pertains, or with which it is most nearly connected, to make and/or use the invention. Applicants respectfully traverse this rejection.

In the Non-Final Rejection mailed May 26, 2010, the Examiner characterizes the sensor film as comprising doped or undoped conductive organic material and conductive material. The Office cites to references that teach layered materials or materials that do not comprise alternating regions of dissimilar material that are transverse to an electrical path.

Applicants' invention recite that the material comprises a conductive organic polymer material (which is either doped or undoped) and a inorganic conductive material (e.g., a conductive inorganic material) or carbon black. Although the graphic depiction provided in the Appeal depicts "ordered" alternating regions, this was solely meant to depict the alternating regions (see, e.g., Figure 1 of Appeal Brief filed November 5, 2004). The regions are not ordered but vary in distance from one another by 10-1,000 Angstroms (see, e.g., page 25, lines 20-24). In addition, the figure was used to in an attempt to depict the "path" being transverse to the alternating regions. To be transverse the Figure depicts the 'interpenetrating' aspect (i.e., the regions penetrate from the surface to the substrate). This alternating interpenetrating language is supported in the specification as previously described. With reference to the distance (i.e., 10-1,000 Angstroms), this language is also supported in the specification as set forth previously.

For at least the foregoing reasons, Applicants respectfully request withdrawal of this rejection.

II. REJECTION UNDER 35 U.S.C. §102

Claims 98, 104-105, 108-110, 112, 115, 117, 120-122, 126-127 and 159 stand rejected under §102(b) as allegedly anticipated by Haugen (Analytical Chemistry 1988). Applicants respectfully traverse this rejection.

In order for a claim to be anticipated the cited reference must teach each and every element of the claim. Haugen does not teach a sensor having regions of an inorganic conductive material or carbon black and a conductive organic polymer material having *alternating regions* separated by about 10-1000 angstroms between two conductive leads. Haugen does not teach gold as a sensing area. Haugen does not teach alternating regions including, for example, gold. Haugen teaches and suggests only a semiconductive material between two leads. As indicated by the Examiner, Haugen teach "layers" (see, e.g., page 3, lines 12-20 of the Final Office Action): "In that section it is taught that very thin *layers* of semiconductor material exhibit substantial changes. . . when even a fractional *monolayer*. . . are deposited on them." Furthermore, Figure 5 of Haugen states that the gold microcrystal are "*on a thin layer* of phthalocyanine." This again demonstrates that lack of interpenetrating regions (i.e., a current could not be transverse to the alternating regions).

Thus, Haugen does not teach or suggest alternating regions transverse to the electrical path. In the absence of the alternating regions transverse to the electrical path (i.e., alternating interpenetrating regions) the chemiresistor would not function in the same manner as Applicants' claimed invention. Accordingly, Haugen cannot anticipate Applicants' claimed invention.

IV. REJECTION UNDER 35 U.S.C. §103

Claims 99, 101, 106-107, 113, 128-135, 137, 139 and 142-158 stand rejected under 35 U.S.C. §103 as allegedly unpatentable over Haugen (above) and further in view of Gibson or Lewis. Applicants respectfully traverse this rejection.

Haugen was addressed above and does not teach alternating regions of an inorganic conductive material or carbon black and a conductive organic polymer material. Lewis also does not teach or suggest alternating regions of a conductive organic polymer material and an inorganic conductive material or carbon black. Gibson also do not teach or suggest alternating regions of an inorganic conductive material or carbon black and a conductive organic polymer material. The Examiner points to the terms "copolymer" and "blends" as allegedly teaching alternating regions. However, as repeatedly pointed out in the prior responses and on appeal, a copolymers when polymerized do not form to separate materials but become a

single material; blends of monomers for polymers. Furthermore, a "doped" polymer is not the same as alternating regions of an inorganic conductive material or carbon black and a conductive organic polymer material transverse to the electrical path.

The combination of Haugen and Gibson fails to teach or suggest alternating regions of an inorganic conductive material or carbon black and a conductive organic polymer material transverse to the electrical path.

The addition of Lewis fails to remedy the deficiencies of Haugen and Gibson. Lewis does not teach a sensor comprising an inorganic conductive material or carbon black and a conductive organic polymer material. Lewis teach sensor comprising insulating components.

For, at least, the foregoing reasons the claims submitted herewith are non-obvious over the references either alone or in combination.

Claims 100, 102-103, 113, 117-121, 123, 135 and 139-143 stand rejected as allegedly unpatentable over Haugen or Haugen in view of Gibson or Lewis as above and further in view of Stetter or Wampler. Applicants respectfully traverse this rejection.

Haugen, and Haugen in view of Lewis or Gibson, were addressed above. The addition of Wampler does not remedy the deficiencies above.

Wampler teaches that polypyrrole composites are useful for eliminating Cr(VI) in the environment by reducing Cr(VI) to Cr(III) (see, e.g., page 1820). Wampler does not teach or suggest sensors and sensor systems. There is absolutely no reason why one of skill in the art would consider this reference in arriving at a sensor material. The reference is directed to a purpose that has nothing to do with sensors, particularly resistometric sensors. There is no teaching or suggestion that any material in Wampler would be useful as a material in either an amperometric-electrochemical sensor system or in a conductimetric/resistometric sensor system. Applicants respectfully submit that the addition of Wampler, which has nothing to do with sensor systems, is based upon hindsight reconstruction, wherein the Office is picking and choosing among references that have no bearing on sensor systems to arrive at Applicants' invention. Such hindsight reconstruction and picking and

choosing among references where there is no suggestion in the art for such combination cannot be done.

Furthermore, Wampler do not teach or suggest alternative regions of material wherein one comprises a doped conductive organic polymer material and one is an inorganic conductive material or carbon black. Again, this reference fails for at least the same reasons identified above with respect to Haugen, Lewis, and Gibson.

Stetter teaches the use of a chemiresistive layer comprising a mixture of conductive particles and an elastomer/polymer (see, column 3, lines 5-9). Various polymers are identified at column 4, lines 49-55, and consist of ethylene propylene, styrene butadiene, silicone, fluorsilicone, butyl rubber, isobutylene isoprene, chloroprene, fluorocarbon and polyacrylate, all commonly used *insulating* polymers. Thus, Stetter does not teach a mixture of two compositionally different *conductive* materials, but to the contrary teaches and suggests only mixtures of conductive material and non-conductive material. This is cumulative to Lewis (addressed above).

Claims 114, 116, 136, 138 and 158 stand rejected as allegedly unpatentable over Haugen, or Haugen in view of Gibson or Lewis (as above), and further in view of Mifsud I and II (USP 5,801,297 and WO 95/08113, respectively). Applicants respectfully traverse this rejection.

Mifsud I and II are cumulative and teach that polymer sensors are less sensitive than semiconductive sensors (see, e.g., column 1, lines 62-64). In order to overcome this lack of sensitivity Mifsud I and II combine *different sensor types* (e.g., semiconductive sensors, polymer sensors, and surface-acoustic-wave sensors). Mifsud I and II teach combining sensor types **not** changing sensor materials. Mifsud I described the advantages of Mifsud's invention at column 3, lines 22-32:

The point of this . . . is to provide. . . three different means of detection in order to obtain better sensitivity and better general selectivity of detection. In fact, as has been explained at the beginning of the description, the different types of sensors, with semiconductive, conductive polymer or surface acoustic wave technology, each have different characteristics which are complementary: good sensitivity (semiconductive sensors), good selectivity (conductive-polymer sensors), and good mass/volume measurement (surface-acoustic-wave sensors). (emphasis ours)

Accordingly, the addition of Mifsud I and/or II does not remedy the deficiencies of the prior references.

Claims 98-99, 101, 104-110, 112-113, 115, 117, 120-122, 126-135, 137, 139 and 142-159 are allegedly unpatentable over Gibson (as described above) in view of Haugen (as above) and Barisci (Trends in Polymer Science, 1996). Applicants respectfully traverse.

As the Board recognized the differences in amperometric and resistometric sensors are significant in their operation. The fact that a polypyrrole amperometric sensor change chemically is due to "poisoning" which is a bad thing. One of skill in the art would not look to the "poisoning" of a material as a good thing in a resistometric sensor (i.e., "poisoning" is an undesirable aspect of both resistometric and amperometric sensors). Furthermore, the "oxidation" or "reduction" of an amperometric material is due to changes in the electrolyte solution (not due to the actual analyte being contacted with the sensor material). The oxidation/reduction of the electrolyte solution causes electron flow through and amperometric system (i.e., the electrons flow due to the oxidation/reduction. In contrast, resistometric sensor systems cause electron flow by a power source.

The fact that Barisci describes amperometric sensors and resistometric sensor general operations does not remedy the deficiencies of the prior references. In fact, the additional of Barisci appears to be derived by the Office performing hindsight reconstruction. For example, the hindsight reconstruction to combine the teachings at page 15, first full paragraph, makes little sense. There is absolute no suggestion in any of the references of a desirability to "reduce the resistivity of the organic conductor materials" or that such a "reduction" in resistance would facilitate a "more reasonable [detection] condition".

Even with the addition of Barisci the combination still fails to set forth a *prima facie* case of obviousness since the combination fails to teach or suggest the combination of the sensor materials as set forth in Applicants' independent claims including, but not limited to, alternating regions of different materials transverse to the electrical path.

Claims 100, 102-103, 113, 117-121, 123, 135 and 139-143 are allegedly unpatentable over Gibson in view of Haugen and Barisci as applied above, and further in view of Lewis, Stetter or Wampler. Applicants respectfully traverse this rejection.

Each of the references and various combinations thereof have been addressed above. Briefly, Gibson does not teach or suggest combination of an inorganic conductive material or carbon black and an organic conductive polymer material. Haugen and Gibson do not teach or suggest combination comprising regions of an inorganic conductive material or carbon black and an organic conductive polymer material transverse to the electrical path. Gibson, Haugen and Barisci do not teach or suggest combination of an inorganic conductive material or carbon black and an organic conductive polymer material. Gibson, Haugen, Barisci and Lewis, Stetter or Wampler do not teach or suggest combination comprising regions of an inorganic conductive material or carbon black and an organic conductive polymer material transverse to the electrical path. Layers of material with different materials would NOT function in the manner of Applicants' invention.

Claims 114, 116, 136, 138 and 158 are allegedly unpatentable over Gibson in view of Haugen and Barisci and further in view of Mifsud I and/or II. Applicants respectfully traverse this rejection.

Each of the references and various combinations thereof have been addressed above. Briefly, Gibson does not teach or suggest combination of an inorganic conductive material and an organic conductive polymer material. Haugen and Gibson do not teach or suggest combination of an inorganic conductive material or carbon black and an organic conductive polymer material. Gibson, Haugen and Barisci do not teach or suggest combination of an inorganic conductive material or carbon black and an organic conductive polymer material. Gibson, Haugen, Barisci and Mifsud I and/or II do not teach or suggest combination of an inorganic conductive material or carbon black and an organic conductive polymer material.

For at least the foregoing, the Applicant submits that the claimed invention is patentable and request reconsideration and notice of such allowable subject matter.

The Director is authorized to charge any required fee or credit any overpayment to Deposit Account Number 50-4586, please reference the attorney docket number above.

The Examiner is invited to contact the undersigned at the below-listed telephone number, if it is believed that prosecution of this application may be assisted thereby.

Respectfully submitted,

GAVRILOVICH, DODD & LINDSEY LLP

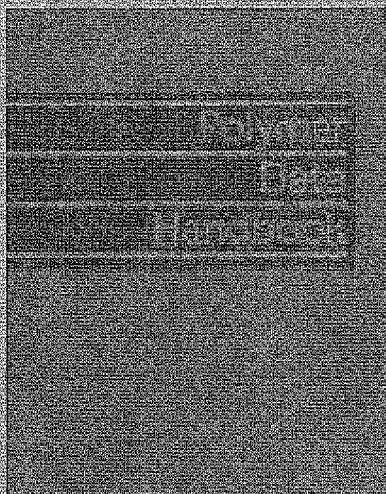
Date: January 26, 2012

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POLYMER DATA HANDBOOK

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EXHIBIT A

EDITED BY JAMES E. MARK, UNIVERSITY OF CINCINNATI

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The online version of the *Polymer Data Handbook* includes key data on over two hundred polymers. Please note that entries are presented as PDF files and can only be read using Adobe Acrobat Reader Version 3. If you do not have the freeware reader, it can be downloaded from [Adobe in the United States](#) or [Adobe in the United Kingdom](#). Each entry opens with a citation of the contributor's name and notations of acronyms and trade names, class of polymer, structure, and major applications. These are followed by tabular displays showing the properties of each polymer. The maximum consistency possible has been established for properties presented with regard to format, terminology, notations, and units. However, not all properties are applicable to all polymers contained in the handbook; some properties may not even be relevant for certain polymer classes. Also, some polymers exhibit properties shown by few others (e.g., electroluminescence); these properties have been noted as "Properties of Special Interest." Each entry closes with a list of references for the reader interested in further investigation of a polymer.

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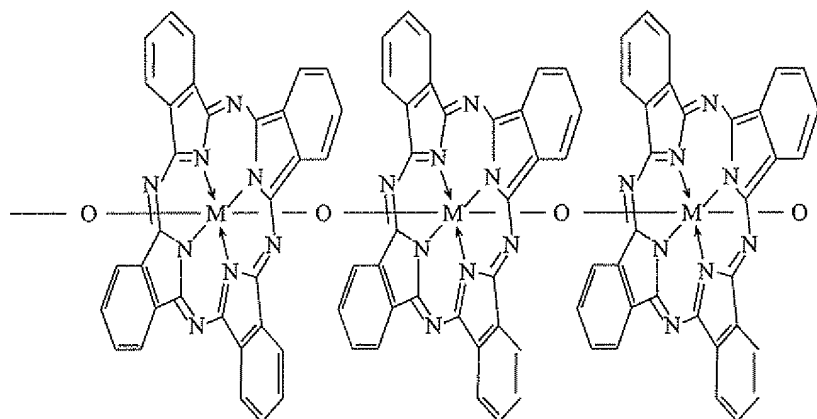
Metallophthalocyanine polymers

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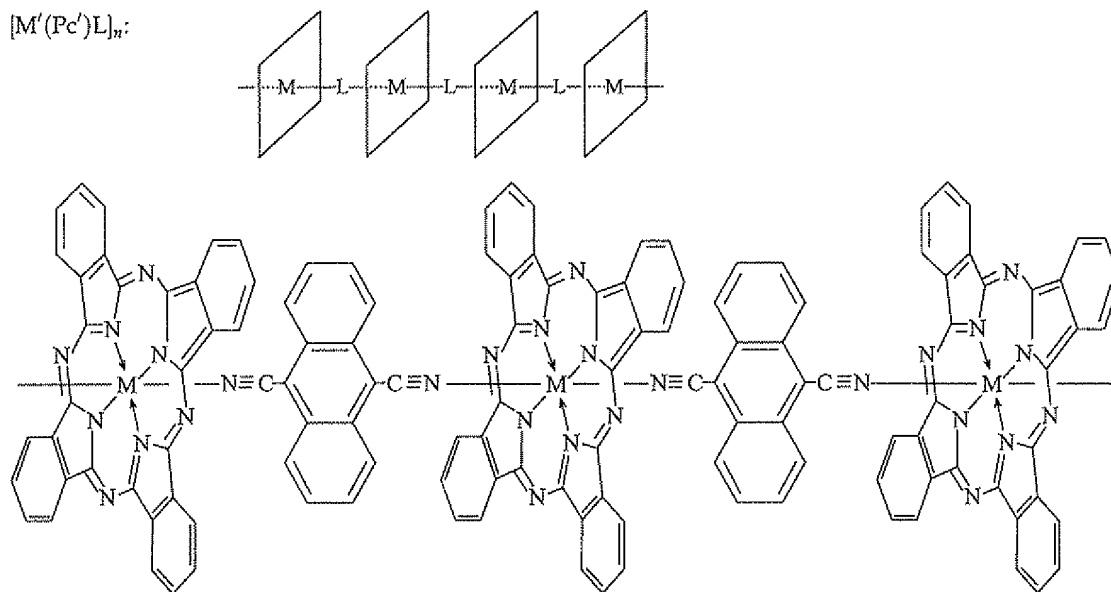
STRUCTURES

$[M(Pc)O]_n$:



where $M = \text{Si, Ge, or Sn}$; Pc = phthalocyanine.

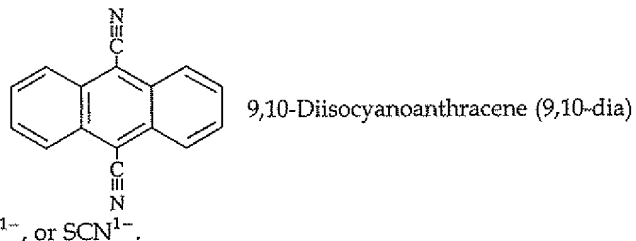
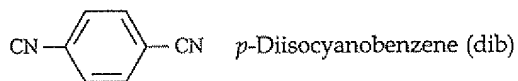
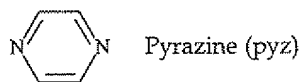
$[M'(Pc')L]_n$:



where $M' = \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Co}^{2+}, \text{Co}^{3+}, \text{Ru}^{2+}, \text{Mn}^{2+}, \text{Mn}^{3+}, \text{or Cr}^{3+}$.

Metallophthalocyanine polymers

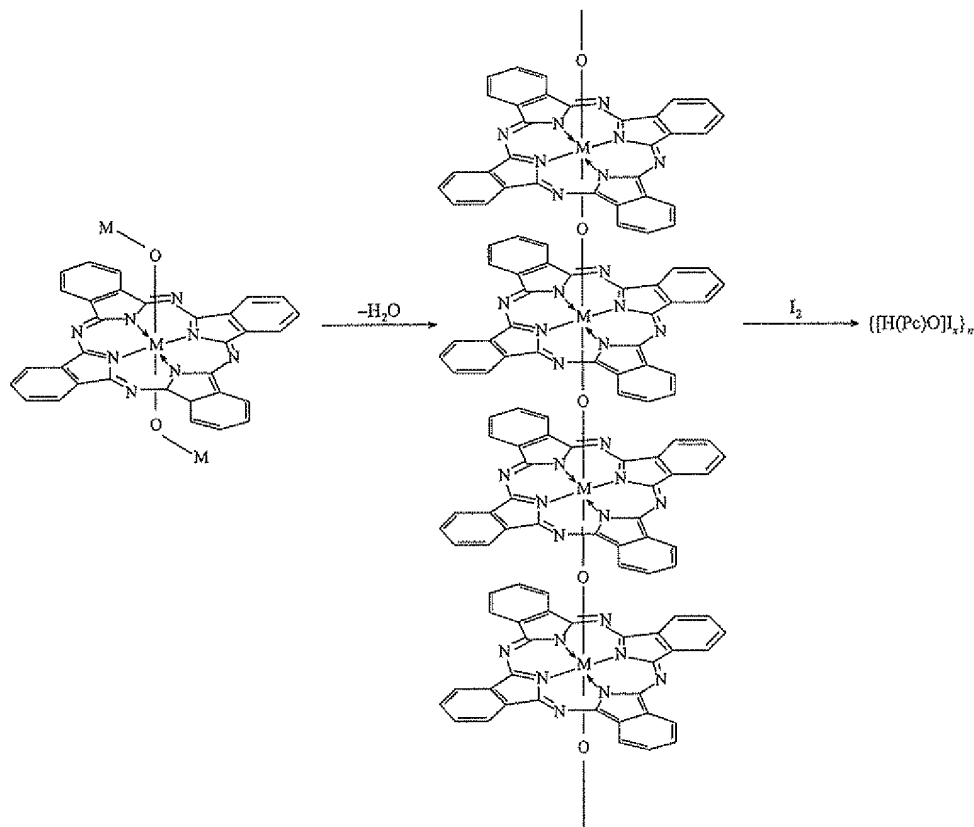
L =



CN¹⁻, or SCN¹⁻.

Pc' = Pc²⁻, R₄Pc²⁻, R₈Pc²⁻, 1,2-Nc²⁻ (1,2-naphthalocyaninato), 2,3-Nc²⁻ (2,3-naphthalocyaninato), or TBP²⁻. R = *t*-Bu, Et, OR' (R' = C₅H₁₁–C₁₂H₂₅) (substituted in the peripheral positions).

SYNTHESIS Condensation of Si(Pc)(OH)₂, Ge(Pc)(OH)₂, Sn(Pc)(OH)₂ to form phthalocyaninato polysiloxanes, polygermyloxanes, and polystannyloxanes.⁽¹⁻⁴⁾



MAJOR APPLICATIONS Electrical conductors, semiconductors, and materials with photooptical properties.

Electric conductivity

POLYMER	UNITS	y	VALUE	REFERENCE
$[\text{Si}(\text{Pc})\text{O}]_n$	$\sigma_{\text{RT}} \text{ ohm}^{-1} \text{ cm}^{-1}$	Nondoped	3×10^{-8}	(5)
	$\sigma (300 \text{ K}) \text{ ohm}^{-1} \text{ cm}^{-1}$	Nondoped	5.5×10^{-6}	(6)
$\{\text{Si}(\text{Pc})\text{O}\}\text{I}_y\}_n$	$\sigma_{\text{RT}} \text{ ohm}^{-1} \text{ cm}^{-1}$	0.50	2×10^{-2}	(5)
		1.40	2×10^{-1}	(5)
		4.60	1×10^{-2}	(5)
$\{\text{Si}(\text{Pc})\text{O}\}(\text{I}_3)_y\}_n$	$s (300 \text{ K}) \text{ ohm}^{-1} \text{ cm}^{-1}$	0.37	5.8×10^{-1}	(6)
$\{\text{Si}(\text{Pc})\text{O}\}\text{Br}_y\}_n$	$\sigma_{\text{RT}} \text{ ohm}^{-1} \text{ cm}^{-1}$	1.00	6×10^{-2}	(5)
$\{\text{Si}(\text{Pc})\text{O}\}\text{BF}_{4y}\}_n$	$\sigma (300 \text{ K}) \text{ ohm}^{-1} \text{ cm}^{-1}$	0.00 ^(a)	3.0×10^{-4}	(7)
		0.00 ^(b)	2.2×10^{-6}	(7)
		0.11	3.7×10^{-3}	(6)
		0.13	3.3×10^{-3}	(7)
		0.18	2.4×10^{-2}	(6)
		0.19	1.4×10^{-2}	(7)
		0.20	5.3×10^{-2}	(6)
		0.27	2.9×10^{-2}	(7)
		0.28	6.7×10^{-2}	(6)
		0.31	9.0×10^{-2}	(6)
		0.36	1.8×10^{-1}	(7)
		0.36	8.6×10^{-2}	(6)
		0.41	1.2×10^{-1}	(7)
		0.50	1.3×10^{-1}	(7)
$\{\text{Si}(\text{Pc})\text{O}\}\text{TOS}_y\}_n$		0.10	5.6×10^{-4}	(7)
(TOS = <i>p</i> -toluenesulfonate)		0.19	1.0×10^{-2}	(7)
		0.28	2.0×10^{-2}	(7)
		0.37	3.7×10^{-2}	(7)
		0.52	4.5×10^{-2}	(7)
		0.67	4.3×10^{-2}	(7)
$\{\text{Si}(\text{Pc})\text{O}\}\text{SO}_{4y}\}_n$		0.040	8.5×10^{-3}	(7)
		0.095	8.8×10^{-2}	(7)
$\{\text{Si}(\text{Pc})\text{O}\}\text{PF}_{6y}\}_n$	$\sigma (300 \text{ K}) \text{ ohm}^{-1} \text{ cm}^{-1}$	0.08	1.3×10^{-2}	(6)
		0.18	1.7×10^{-2}	(6)
		0.20	2.3×10^{-2}	(6)
		0.32	7.8×10^{-2}	(6)
$\{\text{Si}(\text{Pc})\text{O}\}\text{SbF}_{6y}\}_n$	$\sigma (300 \text{ K}) \text{ ohm}^{-1} \text{ cm}^{-1}$	0.39	1.5×10^{-1}	(6)
$\{\text{Ge}(\text{Pc})\text{O}\}_n$	$\sigma_{\text{RT}} \text{ ohm}^{-1} \text{ cm}^{-1}$	Nondoped	$< 10^{-8}$	(5)
$\{\text{Ge}(\text{Pc})\text{O}\}\text{I} - y\}_n$	$\sigma_{\text{RT}} \text{ ohm}^{-1} \text{ cm}^{-1}$	1.80	3×10^{-2}	(5)
		1.90	5×10^{-2}	(5)
		1.94	6×10^{-2}	(5)
		2.0	1×10^{-1}	(5)
$[\text{Sn}(\text{Pc})\text{O}]_n$	$\sigma_{\text{RT}} \text{ ohm}^{-1} \text{ cm}^{-1}$	Nondoped	$< 10^{-8}$	(5)
$\{[\text{Sn}(\text{Pc})\text{O}]\text{I}_y\}_n$	$\sigma_{\text{RT}} \text{ ohm}^{-1} \text{ cm}^{-1}$	1.2	1×10^{-6}	(5)
		5.5	2×10^{-4}	(5)

Metallophthalocyanine polymers

POLYMER	UNITS	γ	VALUE	REFERENCE
{[Fe(Pc)pyz]I _y } _n	σ_{RT} ohm ⁻¹ cm ⁻¹	0 ^(c)	7.79×10^{-8}	(8)
		0.19 ^(d)	9.31×10^{-4}	(8)
		0.38 ^(d)	2.58×10^{-3}	(8)
		0.77 ^(d)	8.63×10^{-3}	(8)
		2.10 ^(d)	7.55×10^{-3}	(8)
		2.76 ^(d)	2.33×10^{-2}	(8)
		0.38 ^(e)	4.60×10^{-4}	(8)
		1.49 ^(e)	5.99×10^{-3}	(8)
		2.10 ^(e)	1.28×10^{-1}	(8)
		2.54 ^(e)	1.90×10^{-1}	(8)
[Fe(Pc)tz] _n	σ_{RT} ohm ⁻¹ cm ⁻¹	Nondoped ^(f)	2×10^{-2}	(9)
[Ru(Pc)tz] _n		Nondoped ^(f)	1×10^{-2}	(9)
[Fe(Pc)Me ₂ tz] _n		Nondoped ^(f)	4×10^{-3}	(9)
[Ru(Pc)(NH ₂) ₂ tz] _n		Nondoped ^(f)	4×10^{-3}	(9)
[Ru(Pc)p-(NH ₂)C ₆ H ₄] _n		Nondoped ^(f)	5×10^{-9}	(9)
[Ru(Pc)Cl ₂ tz] _n		Nondoped ^(f)	3×10^{-3}	(9)
[Os(Pc)pyz] _n		Nondoped ^(f)	1×10^{-6}	(9)
[Os(Pc)tz] _n		Nondoped ^(f)	1×10^{-2}	(9)
[Fe(Me ₈ Pc)pyz] _n		Nondoped ^(f)	3×10^{-9}	(9)
[Fe(Me ₈ Pc)tz] _n		Nondoped ^(f)	1×10^{-2}	(9)
[Ru(Pc)Me ₂ tz] _n		Nondoped ^(f)	4×10^{-3}	(9)
[Fe(CN ₄ Pc)pyz] _n		Nondoped ^(f)	5×10^{-9}	(9)
[Fe(CN ₄ Pc)tz] _n		Nondoped ^(f)	1×10^{-6}	(9)
[Fe(2,3-Nc)pyz] _n		Nondoped ^(f)	5×10^{-5}	(9)

(a) Orthorhombic. (b) Tetragonal. (c) Prepared by: $n\text{Fe(Pc)} + n(\text{pyz}) \xrightarrow{\text{C}_6\text{H}_5\text{Cl or benzene}} [\text{Fe(Pc)(pyz)}]_n$.

(d) Prepared by: $[\text{Fe(Pc)(pyz)}]_n + (ny/2)\text{I}_2 \xrightarrow{\text{benzene}} \{[\text{Fe(Pc)(pyz)}]_y\text{I}_y\}_n$.

(e) Prepared by: $n[\text{Fe(Pc)(pyz)}]_n + (ny/2)\text{I}_2 \xrightarrow{\text{CHCl}_3} \{[\text{Fe(Pc)(pyz)}]_y\}_n + n(\text{pyz})$.

(f) Room temperature, pressed pellets, 1 kbar.

Thermoelectric power⁽⁷⁾

Polymer	γ	S (300 K) ^(a) ($\mu\text{V K}^{-1}$)	$(\Delta S/\Delta T) \sim 300$ (mV K ⁻²)	$4r^{(b)}$ (eV)
{[Si(Pc)O]BF _{4y} } _n	0.13	113		
	0.19	62.9		
	0.27	43.4	0.101	2.70
	0.36	10.5	0.134	1.16
	0.41	4.6	0.135	0.81
	0.50	0.31	0.100	0.70
{[Si(Pc)O]TOS _y } _n	0.10	284		
	0.19	114		
	0.28	82.1	0.079	4.2
	0.37	50.9	0.115	1.27
	0.52	28.2	0.109	0.63
	0.67	26.0	0.096	0.36
{[Si(Pc)O]SO _{4y} } _n	0.095	48.6	0.17	3.8

(a) $S_{\text{sample}} = (\text{Slope of voltage} \sim \text{temp. data}) (S_{\text{thermocouple}}) + S_{\text{gold}}$.

(b) Tight-binding bandwidth derived from a fit to: $S = [2\pi^2 k_B^2 T \cos(\pi\rho/2)]/[3e(4t) \sin^2(\pi\rho/2)]$.

Static magnetic susceptibility

Polymer	y	$\chi_{\text{Pauli}}^{(a)}$ (10^{-4} emu mol $^{-1}$)	Pauli-like spins/M(Pc) $^{(b)}$	A (10^{-4})	α	Curie-like spins/M(Pc) $^{(c)}$	Reference
{[Si(Pc)O]BF $_{4y}$] $_n$ }	0.11	0.68	0.05	135	0.82	0.10	(7)
	0.19	1.40	0.11	16	0.67	0.13	(7)
	0.26	2.39	0.19	101	0.83	0.07	(7)
	0.35	2.22	0.18	92	1.00	0.024	(7)
	0.43	2.28	0.18	90	1.00	0.024	(7)
	0.50	2.32	0.18	83	1.00	0.022	(7)
{[Si(Pc)O]TOS $_y$] $_n$ }	0.67	3.13	0.25	124	1.00	0.032	(7)
{[Si(Pc)O]SO $_{4y}$] $_n$ }	0.095	1.93	0.15	116	0.82	0.09	(7)
{[Si(Pc)O]BF $_{4y}$] $_n$ }	0.36	2.22	0.18	—	—	—	(6)
{[Si(Pc)O]PF $_{6y}$] $_n$ }	0.36	2.49	0.19	—	—	—	(6)
{[Si(Pc)O]SbF $_{6y}$] $_n$ }	0.36	2.22	0.18	—	—	—	(6)
{[Si(Pc)O](I $_3$) $_y$] $_n$ }	0.37	2.35	0.18	—	—	—	(6)
{[Ge(Pc)O](I $_3$) $_y$] $_n$ }	0.37	2.70	0.21	—	—	—	(6)

(a) For $\chi = \chi_{\text{Pauli}} + AT^{\alpha}$.(b) $N_p = 3\chi_{\text{Pauli}}kT/Ng^2\mu_B^2S(S+1)$, where $T = 298$ K.(c) $N_c = 3AT^{1-\alpha}k/Ng^2\mu_B^2S(S+1)$, where $T = 298$ K.

Unit cell dimensions

Polymer	y	Space group	Z	Cell dimensions (Å)			Interplanar spacing (Å)	Staggering angle ϕ (degrees)	Reference
				a	b	c			
[Si(Pc)O] $_n$	—	Ibam	4	13.80	27.59	6.66	3.33	39	(5)
[Ge(Pc)O] $_n$	—	P4/m	1	13.27	3.53	—	3.53	0	(5)
—	—	I4/m	2	18.76	3.57	—	3.57	0	(5)
[Sn(Pc)O] $_n$	—	P4/m	1	12.81	3.8	—	3.82	Probably eclipsed	(5)
[Ga(Pc)F] $_n$	—	PI	—	3.871	12.601	12.793	3.87	Probably eclipsed	(5)
{[Si(Pc)O]BF $_{4y}$] $_n$ }	0.36	P4/mcc	2	13.70	—	6.58	3.29	40	(6, 7)
	0.50	P4/mcc	2	13.96	—	6.66	—	—	(7)
{[Si(Pc)O]PF $_{6y}$] $_n$ }	0.36	P4/mcc	2	13.98	—	6.58	3.29	40	(6, 7)
	0.47	P4/mcc	2	14.08	—	6.63	—	—	(7)
{[Si(Pc)O]SbF $_{6y}$] $_n$ }	0.36	P4/mcc	2	14.31	—	6.58	3.29	40	(6, 7)
	0.41	P4/mcc	2	14.19	—	6.61	—	—	(7)
{[Si(Pc)O](I $_3$) $_y$] $_n$ }	0.37	P4/mcc	2	13.97	—	6.60	3.30	39	(6)
{[Si(Pc)O](Br $_3$) $_y$] $_n$ }	0.37	P4/mcc	2	13.97	—	6.60	3.30	39	(6)
{[Ge(Pc)O](I $_3$) $_y$] $_n$ }	0.36	P4/mcc	2	13.96	—	6.96	3.48	40	(6)
{[Si(Pc)O]TOS $_y$] $_n$ }	0.67	P4/mcc	2	14.39	—	6.64	—	—	(7)
{[Si(Pc)O]PYS $_y$] $_n$ }	0.22	P4/mcc	2	13.70	—	6.65	—	—	(7)
{[Si(Pc)O](CF $_3$ SO $_3$) $_y$] $_n$ }	0.55	P4/mcc	2	13.99	—	6.60	—	—	(7)
{[Si(Pc)O]SO $_{4y}$] $_n$ }	0.095	P4/mcc	2	13.86	—	6.67	—	—	(7)
{[Si(Pc)O]NFBS $_y$] $_n$ }	0.36	P4/mcc	2	14.37	—	6.63	—	—	(7)
{[Si(Pc)O]PFOS $_y$] $_n$ }	0.26	P4/mcc	2	13.91	—	6.61	—	—	(7)

Metallophthalocyanine polymers

Other physical properties⁽⁴⁾

PROPERTY	POLYMER	CONDITIONS
Color	[Si(Pc)O] _n	Dark purple powder
Solubility	[Si(Pc)O] _n	Concentrated H ₂ SO ₄ and HSO ₃ CH ₃ : 0.013 g in 25 ml concentrated H ₂ SO ₄ at room temperature 0.020 g in 25 ml concentrated H ₂ SO ₄ at 80°C

Densities

POLYMER	y	DENSITY (G CM ⁻³)		REFERENCE
		CALCULATED	FOUND	
[Si(Pc)O] _n	—	1.458	1.432	(4, 6)
[Ge(Pc)O] _n	—	1.609 ^(a)	1.512	(4, 6)
	—	1.589 ^(b)	—	(4, 6)
[Sn(Pc)O] _n	—	1.715	1.719	(4, 6)
{[Si(Pc)O]BF ₄ } _n	0.36	1.581	1.545	(6)
{[Si(Pc)O]PF ₆ } _n	0.36	1.573	1.563	(6)
{[Si(Pc)O]SbF ₆ } _n	0.36	1.582	1.591	(6)
{[Si(Pc)O](I ₃) _y] _n	0.37	1.802	1.744	(6)
{[Ge(Pc)O](I ₃) _y] _n	0.36	1.805	1.774	(6)

^(a)Space group: *P4/m*; *Z* = 1; *a* = 13.27, *c* = 3.53.

^(b)Space group: *I4/m*; *Z* = 2; *a* = 18.76, *c* = 3.57.

Infrared spectroscopy⁽⁴⁾

POLYMER	IR SPECTRAL DATA (CM ⁻¹)*
[Si(Pc)O] _n	530(m), 575(m), 646(w), 721(vs), 759(vs), 762(w), 804(w), 869(vw), 910(s), 936(vw), 1000(bd), 1043(m), 1080(vs), 1121(vs), 1164(s), 1170(sh), 1192(w), 1289(s), 1334(vs), 1351(m), 1426(vs), 1517(s), 1596(w), 1614(m)
[Ge(Pc)O] _n	425(vw), 435(vw), 508(m), 572(m), 640(w), 660(vw), 725(vs), 753(m), 762(vw), 772(vw), 801(w), 865(bd), 899(s), 935(vw), 945(vw), 970(vw), 998(w), 1068(vs), 1087(vs), 1119(vs), 1162(s), 1195(w), 1284(m), 1332(vs), 1345(m), 1419(s), 1500(m), 1588(w), 1612(m)
[Sn(Pc)O] _n	428(w), 435(sh), 495(m), 570(m), 640(w), 660(vw), 687(vw), 716(vs), 750(s), 762(m), 769(m), 775(sh), 808(m), 825(bd), 872(w), 888(m), 950(w), 1005(vw), 1058(s), 1089(s), 1120(vs), 1168(m), 1183(w), 1263(w), 1284(m), 1293(w), 1338(vs), 1405(sh), 1580(sh), 1610(m)

*Peaks not readily assigned to M(Pc) moiety; s = strong, m = medium, w = weak, bd = broad, sh = shoulder, v = very.

Optical spectroscopy⁽⁴⁾

COMPOUND	ABSORPTION MAXIMUM (NM)
[Si(Pc)O] _n	203, 285, 335, 625
[Ge(Pc)O] _n	285, 350, 645
[Sn(Pc)O] _n	205, 290, 365, 655, 695

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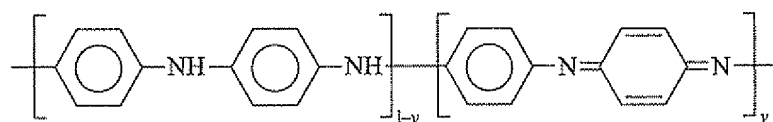
Polyaniline

STEPHEN S. HARDAKER AND RICHARD V. GREGORY

ACRONYM, ALTERNATIVE NAMES, TRADE NAMES PANI, emeraldine, leucoemeraldine, pernigraniline, Ormecron (Zipperling Kessler and Co.), Zypan (Du Pont)

CLASS Conjugated and other unsaturated polymers; electrically conductive polymers

STRUCTURE Polyaniline base of variable oxidation state

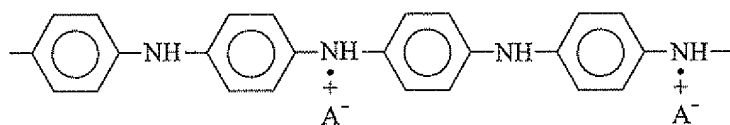


$y = 0$: Leucoemeraldine base (LEB)

$y = 0.5$: Emeraldine base (EB)

$y = 1$: Pernigraniline base (PNB)

Emeraldine salt (ES)



MAJOR APPLICATIONS Polyaniline is finding widespread use in novel organic electronic applications such as: light emitting diodes (LED), electroluminescence, metallic corrosion resistance, organic rechargeable batteries, biological and environmental sensors, composite structures, textile structures for specialized applications or static dissipation, membrane gas-phase separation, actuators, EMI shielding, organic semiconductor devices for circuit applications, blends with insulative host polymers to impart a slight electrical conductivity, bioelectronic medical devices, and a variety of other applications where tunable conductivity in an organic polymer is desirable.

PROPERTIES OF SPECIAL INTEREST Electrical conductivity in the range of 10^{-8} to 400 S cm^{-1} . This conductivity will increase as better processing methods are developed reducing structural defects. The conductivity can be tuned to specific end uses for a variety of applications. Polyaniline is reasonably stable under ambient conditions and, with the proper selection of dopants, retains its conductivity over long periods of time (i.e., five years and longer). Polyaniline easily switches from the conductive form (emeraldine salt) to the insulative form (emeraldine base) as a function of pH. Under acidic conditions the polymer acid dopes and becomes conductive. When exposed to higher pH levels the polymer switches to the insulative form. This facile switching can be cycled many times.

Polyaniline

Unit cell dimensions⁽¹⁾

Form	a (Å)	b (Å)	c (Å)	Lattice	Comments
EB-II	7.80	5.75	10.05	Orthorhombic	NMP-cast, stretched film
	7.65	5.75	10.20	Orthorhombic	THF/NMP-extracted powder
	7.65	5.65	10.40	Orthorhombic	Powder from THF-extracted solution
ES-II	7.1	7.9	10.4	Orthorhombic	NMP-cast, stretched film, HCl dopant
	7.0	8.6	10.4	Orthorhombic	THF/NMP-extracted powder, HCl dopant
ES-I	4.3	5.9	9.6	Pseudoorthorhombic	As synthesized, HCl dopant

Solubility parameters of polyaniline and several solvents

Compound	δ (MPa ^{1/2})	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})	Comment	Reference
Emeraldine base	22.2	17.4	8.1	10.7	Empirical	(2)
Emeraldine salt	23.6	17	8.9	13.7	Empirical	(2)
Leucoemeraldine base	23–25	21.1	5.6	7.3	Empirical	(2)
1-Methyl-2-pyrrolidinone (NMP)	23.7	16.5	10.4	13.5	Calculated	(2)
N,N'-dimethyl propylene urea (DMPU)	22.3	16.4	11.3	10.0	Calculated	(3)
m-Cresol	22.7	18.7	4.8	13.5	Calculated	(2)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Permeability	$\text{m}^3(\text{STP}) \text{m s}^{-1}$ $\text{m}^{-2} \text{Pa}^{-1}$	Gas		(4)
		H ₂	3,580	
		CO ₂	586	
		O ₂	123	
		N ₂	13.4	
		CH ₄	3.04	
Huggins parameter: k'	—	Form/Solvent		(5)
		EB/NMP	0.384	
		EB/DMPU	0.371	
Storage modulus	MPa	EB form; EB film cast from NMP; DMTA, 1 Hz, 25°C	2,000	(6)
		ES-HCl form; EB film cast from NMP then doped with HCl; DMTA, 1 Hz, 25°C	2,300	
Loss modulus	MPa	EB form; EB film cast from NMP; DMTA, 1 Hz, 25°C	256	(6)
		ES-HCl form; EB film cast from NMP then doped with HCl; DMTA, 1 Hz, 25°C	218	

Mechanical properties of polyaniline fibers

Fiber process ^(a)	Base			Dopant	Doped			Conductivity (S cm ⁻¹)	Reference
	Tenacity (gpd) ^(b)	Modulus (gpd) ^(b)	Elongation (%)		Tenacity (gpd) ^(b)	Modulus (gpd) ^(b)	Elongation (%)		
PANI-CSA/ <i>m</i> -cresol ^(c)	n/a	n/a	n/a	CSA	0.2	7.3	8.4	203	(7)
PANI-EB/H ₂ SO ₄	n/a	n/a	n/a	H ₂ SO ₄	1.8	39.3	25.4	6.3	(7)
PANI-EB/NMP ^(d) drawn	3.9	—	—	HCl	1.4	—	—	160	(8)
PANI-EB/DMPU as-spun	0.2-0.6	27	7	CH ₃ SO ₃ H	<0.2	—	—	10-32	(9)
PANI-EB/DMPU 4× drawn	2.4	56	13	CH ₃ SO ₃ H	<1.0	—	—	350	(9)
PANI-LEB/DMPU as-spun	1.1	57	51	CH ₃ SO ₃ H	0.8	—	—	15	(10)
PANI-LEB/DMPU 2× drawn	3.6	89	15	HCl	1.9	—	—	140	(10)

^(a)Fiber process is designated as: polyaniline form/solvent, post process.

^(b)gpd ≡ g denier⁻¹. Denier is a linear density: 1 denier = 1 g (9,000 m)⁻¹.

^(c)Mixture of emeraldine base and (±)-camphor sulfonic acid dissolved in *m*-cresol.

^(d)Solution also contained a gel inhibitor.

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Room temperature conductivity	S cm ⁻¹	CSA dopant; film cast from <i>m</i> -cresol;	400		(11)
		PANI-CSA complex formed in solution			
		CH ₃ SO ₃ H dopant; fiber spun in EB form	350		(9)
		from DMPU and 4× drawn then doped			
		CSA dopant; as-spun fiber from <i>m</i> -cresol;	203		(7)
		EB and CSA mixed as powder			
		CSA dopant; film cast from 30/70	70		(11)
		chloroform/ <i>m</i> -cresol; EB and CSA			
Apparent bandgap (absorption)	eV	mixed as powder			
		CH ₃ SO ₃ H/acetic acid dopant; film cast	60		(5)
		from EB/DMPU then doped			
		HCl dopant; film cast from EB/NMP and	24		(12)
		4× drawn then doped			
		I ₂ dopant; spin-coated from LEB/DMPU	11.4		(13)
		then doped			
		H ₂ SO ₄ dopant	6.31		(14)
Melting temperature	K	Polyaniline form	Onset	Peak	(11)
		LEB	3.2	3.6	
		EB	1.6 (3.0)	2.0 (3.8)	
		PNB	1.8	2.3	
		LEB film and fiber from DMPU; DSC,	658		(15)

Polyaniline

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Glass transition temperature	K	LEB fiber spun from DMPU; DSC, 5°C min ⁻¹ , N ₂	474	(16)
		EB film cast from NMP; DMTA, 5°C min ⁻¹ , 1 Hz	493	(6)
Sub- <i>T_g</i> transition temperature	K	EB film cast from NMP; DMTA, 3°C min ⁻¹ , 1 Hz; assigned to phenyl ring twisting	193	(17)
Thermal stability	K	Cross-linking reaction; EB film cast from NMP; DMTA, 3°C min ⁻¹ , 1 Hz	453	(17)
		Decomposition (LEB) reaction; LEB spin coated film from DMPU; TGA, 20°C min ⁻¹ , N ₂	780	(15)
		Decomposition (EB) reaction; EB film cast from NMP; TGA, 20°C min ⁻¹ , N ₂	673	(6)
Index of refraction <i>n</i>	—	EB spin-coated from DMPU, average, 1,550 nm	1.85	(18)
Zero- <i>T</i> dielectric constant $\epsilon_{mw}(T \rightarrow 0)$	—	PANI-CSA cast from chloroform	~30	(11)
Dielectric constant ϵ_{mw}	—	PANI-CSA cast from <i>m</i> -cresol, 300 K, 6.5 GHz	-4.5×10^{-4}	(11)
Plasma frequency ω_p	eV	PANI-CSA cast from <i>m</i> -cresol, 300 K	0.016	(11)
Dielectric relaxation time τ	s	PANI-CSA cast from <i>m</i> -cresol, 300 K	1.1×10^{-11}	(11)
Electroluminescence emission peak	nm	Porous Si/PANI-CSA(<i>m</i> -cresol), 0.5 A cm ⁻² current density	800	(19)

Surface energies⁽²⁰⁾

Form	Surface Energy			Comments
	γ (erg cm ⁻²)	γ^d (erg cm ⁻²)	γ^p (erg cm ⁻²)	
EB	44.6	36.9	7.7	NMP cast film
PANI-HCl	63.5	38.7	24.8	NMP cast EB; doped with HCl (pH = 0)

Electrochemical potentials of redox processes in polyaniline

Redox Couple	Potential* (V)	Conditions	Reference
Leucoemeraldine/emeraldine	0.15	vs. Cu/CuF ₂ in NH ₄ F + 2.3HF	(21)
Emeraldine/pernigraniline	0.80	vs. Cu/CuF ₂ in NH ₄ F + 2.3HF	(21)
Leucoemeraldine/emeraldine	0.115	vs. SCE in 1.0 M HCl	(22)
Emeraldine/pernigraniline	0.755	vs. SCE in 1.0 M HCl	(22)

* Reported potentials are average of oxidation and reduction potentials for a given redox couple.

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